

PATENT ABSTRACTS OF JAPAN

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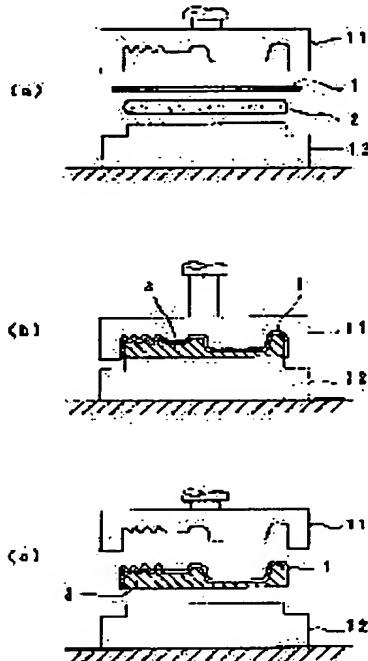
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(54) DECORATIVE MATERIAL AND ITS MANUFACTURE

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a decorative material to be printed clearly and delicately with high flexibility and strength and satisfactory moldability at the time of heating and pressurizing.

SOLUTION: This decorative material is manufactured by preparing a decorative sheet 1 obtained by decorating a base material sheet containing reactive component including monomer or prepolymer chemically bonded by any of addition reaction, condensation reaction or polyaddition reaction with thermosetting resin component molecule in thermoplastic resin, preparing composition 2 containing fibrous reinforcing material in uncured resin of thermosetting resin, then superposing the sheet 1 and the composition 2, heating and pressurizing it in molds 11, 12 of predetermined shape to cure the composition, thereby forming a molding of a predetermined shape, and simultaneously adhesively integrating the sheet with the molding.



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CLAIMS

[Claim(s)]

[Claim 1] It comes to carry out laminating adhesion of the ornament sheet on the front face of the Plastic solid which consists of a hardened material of the thermosetting resin reinforced with fiber reinforcing materials. In thermoplastics this ornament sheet A thermosetting resin component molecule and an addition reaction, It consists of what performed ornament processing to the base material sheet containing the reactant component which consists of the monomer or prepolymer of an organic compound which can carry out a chemical bond by the condensation reaction or the polyaddition reaction. Makeup material characterized by this reactant component and a thermosetting resin component coming to carry out a chemical bond mutually in the interface.

[Claim 2] While preparing the ornament sheet which comes to give ornament processing for the base material sheet containing the reactant component which consists of the monomer or prepolymer which can carry out a chemical bond to a thermosetting resin component molecule by the addition reaction, the condensation reaction, or the polyaddition reaction into thermoplastics The constituent containing fiber reinforcing materials is prepared into the non-hardened material of thermosetting resin. Subsequently By carrying out the adhesion unification of this ornament sheet and this Plastic solid at the same time heat and pressurize these ornament sheet and a non-hardened constituent with the mold of superposition and a predetermined configuration, it makes this constituent harden and it makes it the Plastic solid of a predetermined configuration The process of the makeup material characterized by taking out this layered product from a mold the makeup material which consists of both layered product, nothing, and after an appropriate time.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the makeup material fabricated by SMC (Sheet molding compound), BMC (Bulk molding compound), etc. and its manufacture approach.

[0002]

[Problem(s) to be Solved by the Invention] Although the approach (for example, reference, such as JP,48-12876,A and JP,51-20951,A) of carrying out the shaping coincidence unification of titanium paper, a nonwoven fabric, cloth, the impregnated paper, etc. is conventionally learned as an approach of manufacturing fiber assistant ignition hardenability makeup material (FRP) with a pattern this approach — ** — ** to which does not have ** moldability which cannot perform clear printing, and which ** tear etc. tends to produce, and a configuration is restricted — there is a fault said that the adhesive variation by process conditions, such as temperature and a pressure, is large since it is adhesion of a physical anchor effect.

[0003] Moreover, although the approach of the melting temperature which printed backing a nonwoven fabric with 2 liquid hardening mold polyurethane resin adhesive to the plastic film more than FRP molding temperature, and making this sheet unify at the time of shaping was also taken so that it might be indicated by JP,7-60911,A, by this approach, there was a trouble that the quality of a nonwoven fabric was unstable to the top where the process of backing is complicated, and cost reached it highly by formation nonuniformity etc.

[0004] Moreover, as an option, so that it may be indicated by JP,56-72930,A etc. Although an adhesive property with SMC resin is good, namely, the method of making the makeup sheet using melting, the plastic film which becomes soft, or swells and dissolves of the component of SMC, or printing ink unify at the temperature at the time of SMC shaping at the time of shaping is also learned By this approach, there is a trouble that a printing layer is passed with the heat at the time of heat curing of SMC or the stress at the time of a flow, and a defect comes out.

[0005] Highly, the place which this invention is made in view of the above troubles, and is made into the purpose has a good moldability, and that of adhesion with a Plastic solid and an ornament sheet is good, and the flexibility at the time of heating and pressurization and reinforcement are to offer the makeup material which can perform clear and delicate printing, and its manufacture approach.

[0006]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, the makeup material of this invention It comes to carry out laminating adhesion of the ornament sheet on the front face of the Plastic solid which consists of a hardened material of the thermosetting resin reinforced with fiber reinforcing materials. In thermoplastics this ornament sheet A thermosetting resin component molecule and an addition reaction, It consists of what performed ornament processing to the base material sheet containing the reactant component which consists of the monomer or prepolymer of an organic compound which can carry out a chemical bond by the condensation reaction or the polyaddition reaction. It is characterized by this reactant component and a thermosetting resin component coming to carry out a chemical bond mutually in the interface.

[0007] In thermoplastics the above-mentioned makeup material A thermosetting resin component molecule and an addition reaction, While preparing the ornament sheet which comes to give ornament processing for the base material sheet containing the reactant component which consists of the monomer or prepolymer which can carry out a chemical bond by the condensation reaction or the polyaddition reaction The constituent containing fiber reinforcing materials is prepared into the non-hardened material of thermosetting resin. Subsequently By carrying out the adhesion unification of this ornament sheet and this Plastic solid at the same time heat and pressurize these ornament sheet and a non-hardened constituent with the mold of superposition and a predetermined configuration, it makes this constituent harden and it makes it the Plastic solid of a predetermined configuration It is manufactured by taking out this layered product from a mold the makeup material which consists of both layered product, nothing, and after an appropriate time.

[0008] The reactant component which carries out a chemical bond to the component of a thermosetting resin Plastic solid into the ornament sheet of thermoplastics is made to contain, and the reactant component contained on the sheet carries out reaction adhesion with thermosetting resin, and enables it to unify by this invention as mentioned above in the case of the hardening reaction at the time of shaping.

[0009]

[Embodiment of the Invention] what can bear the heat (a maximum of about 150 degrees C) at the time of shaping (at namely, the time of FRP shaping) as thermoplastics — it is — melting temperature (or melting point) — the

SMC molding temperature — high — in addition — and from the point of a sheet moldability, the following [the SMC molding temperature] have desirable BIKATTO softening temperature. Moreover, what has neither the dissolution nor swelling by the component in SMC is chosen. And what has concealment nature or transparency according to an application is used for a base material sheet. Specifically, fluororesin, such as polyolefines, such as thermoplastic polyester, such as polyethylene terephthalate (PET) which carried out biaxial extension, polybutylene terephthalate (PBT), and polyarylate, polyethylene (PE), a PORIPIRO pyrene (PP), the poly methyl pentene, and thermoplastic elastomer olefin, polyvinyl fluoride, polyvinylidene fluoride, and an ethylene tetrafluoroethylene copolymer, silicon resin, Vynylon, nylon, a polyvinyl chloride (PVC), an acrylic, a polycarbonate, an ethylene-vinylalcohol copolymer, etc. are mentioned. These sheets may use what carried out the laminating more than two-layer also by the monolayer. Sheet thickness is usually about 20–300 micrometers. Although a suitable thing is chosen according to the molding temperature of SMC, and a shaping configuration from these sheets, especially in the case of the curved surface where molding temperature has curvature only in an one direction like a flat surface or a cylindrical shape in 150 degrees C and a shaping configuration, for example, the biaxial extension PET sheet of 25–200-micrometer thickness is suitably used from the point of thermal resistance and reinforcement. Easily-adhesive processing of corona discharge treatment etc., drilling of the micropore for extracting the air between SMC, etc. may be given to these thermoplastics sheets if needed. Moreover, in order to make the weatherability of the sheet itself or FRP [directly under] improve, light stabilizer, such as ultraviolet ray absorbents, such as benzotriazol and particle cerium oxide, and a hindered amine system radical scavenger, may be added in a sheet. [0010] As a monomer, the following are mentioned among the organic compounds contained for a reactant component.

** Vinyl system monomers, such as styrene, alpha-methyl SUCHIN, a divinylbenzene, vinyltoluene, vinyl acetate, and an acrylic acid (meta).

** Monofunctional (meta) acrylate, such as methyl (meta) acrylate, 2-ethylhexyl (meta) acrylate, and phenoxy ethyl (meta) acrylate. Moreover, they are diethylene-glycol (meta) acrylate, propylene GURIKORUJI (meta) acrylate, TORIMECHIRU pro pantry (meta) acrylate, trimethylol propane ethylene OKISAIDOTORI (meta) acrylate, dipentaerythritol PENTA (meta) acrylate, dipentaerythritol hexa (meta) acrylate, etc. as polyfunctional monomer. However, acrylate (meta) is a thing with acrylate or methacrylate.

** Isocyanates, such as tolylene diisocyanate, xylenediisocyanate, hexamethylene di-isocyanate, and isophorone diisocyanate.

** In addition to this.

[0011] As a prepolymer, the following are mentioned among the organic compounds contained for a reactant component.

** Acrylate (meta) prepolymers, such as urethane (meta) acrylate, polyester (meta) acrylate, epoxy (meta) acrylate, and triazine (meta) acrylate.

** The adduct of said isocyanate, a polymer.

** Diallyl phthalate prepolymer.

** The prepolymer which has a cationic polymerization nature functional group. For example, the prepolymer of vinyl ether system resin, such as epoxy system resin, such as a bisphenol mold epoxy resin and a novolak mold epoxy compound, fatty-acid system vinyl ether, and aromatic series system vinyl ether.

** In addition to this.

[0012] What can carry out a chemical bond to the non-hardened component molecule of the thermosetting resin to be used by one reaction of an addition reaction, a condensation reaction, and a polyaddition reaction is chosen from these monomers or pre HORIMA. The example of the combination is shown in Table 1. In addition, generally one and the match of the constituent of the non-hardened material of thermosetting resin are effective. Moreover, although one kind of these reactivity component is good, two or more kinds can also be made to contain.

[0013]

[Table 1]

熱硬化性樹脂	反応性有機化合物
不飽和ポリエステル樹脂	スチレン単量体 不飽和ポリエステルプレポリマー
2液硬化型ポリウレタン樹脂	イソシアネート単量体或いはその付加体、多量体
エポキシ樹脂	エポキシ系樹脂プレポリマー
熱硬化性アクリル樹脂	(メタ)アクリレートの単量体 (メタ)アクリレートのプレポリマー

[0014] as the gestalt of content into the thermoplastics sheet of a reactant organic compound — two kinds, mixing (compatibility-izing) and copolymerization-izing, — it is . A mixed typical example is the case where carried out the reactant organic compound of the polyvinyl chloride, and the monomer or prepolymer of acrylate (meta) is used as thermoplastics, and in the sheet which produced both mixture, since this reactant compound functions as a plasticizer (reaction plasticizer) at the time of unreacted, it is contributed also to improvement in a moldability.

Moreover, as a typical example of copolymerization-izing, the case where carry out copolymerization of both and it considers as acrylonitrile-butadiene-styrene copolymer is mentioned, using a styrene monomer as a reactant organic compound, using an acrylonitrile-butadiene copolymer as thermoplastics. Furthermore, when a thermoplastics sheet and compatibility have the copolymer itself, this copolymer can also be mixed in a thermoplastics sheet. For example, the case where Butadiene Styrene is mixed to this is mentioned, using Pori methacrylic acid methyl as thermoplastics.

[0015] As thermosetting resin, an unsaturated polyester resin, vinyl ester resin, diallyl phthalate resin, heat-curing mold acrylic resin, melamine resin, an epoxy resin, 2 liquid hardening mold polyurethane resin, etc. are mentioned.

[0016] In order to make makeup material (mold goods) from these thermosetting resin, the non-hardened constituent which added various additives to what added the cross linking agent, the polymerization initiator, or the reaction accelerator catalyst to the monomer or prepolymer (oligomer is also included) of these resin first if needed in addition to this with fiber reinforcing materials is prepared. There is a gestalt of SMC or BMC as a gestalt of this non-hardened constituent.

[0017] And as shown in drawing 1 (a), the ornament sheet 1 and the non-hardened constituent 2 are piled up and inserted into the die (a punch 11 and female mold 12) of a predetermined configuration. As shown in drawing 1 (b), a mold is closed and pressurized [heat and], the front face of Plastic solid 3 carries out the adhesion unification of the ornament sheet 1 at the same time it uses the non-hardened constituent 2 as solid Plastic solid 3 bridge formation or by carrying out a polymerization and making it harden, and makeup material as shown in drawing 1 (c) is obtained. In that case, a chemical bond is produced by one reaction of an addition reaction, a polymerization reaction, and a polyaddition reaction in the molecules of the reactant component in the ornament sheet 1, and a non-hardened constituent, it cheats to them, and the adhesive strength between the ornament sheet 1 and Plastic solid 3 is reinforced.

[0018] If SMC which is the typical gestalt of a non-hardened constituent is explained in full detail, the ingredient of SMC will consist of thermosetting resin which kneaded fiber reinforcing agents, such as a glass fiber and a carbon fiber, the catalyst, the bulking agent, the release agent, etc. The thermosetting resin used usually has the typical prepolymer of unsaturated polyester. As a fiber reinforcing agent, the staple fiber of a glass fiber is usually used. The content of this glass fiber is usually 10 – 70 % of the weight. As a bulking agent, powder, such as a calcium carbonate, a barium sulfate, and an aluminum hydroxide, is used. Zinc stearate etc. is used as a release agent. In addition, pigments, such as hardening accelerator catalysts, such as polymerization initiators (curing catalyst), such as cross linking agents, such as reaction diluents, such as a styrene monomer and a polyfunctional acrylate (or methacrylate) monomer, isocyanate, and an amine, a benzoyl peroxide, methyl ethyl ketone peroxide, t butyl par PENZO eight, and an organic sulfonate, naphthenic-acid cobalt, and manganese naphthenate, a titanium dioxide, and carbon black, etc. are added if needed.

[0019] Although the ornament processing performed to a base material sheet is possible also for kneading and giving coloring agents, such as a color and a pigment, to this sheet itself, generally gravure, silk screen printing, etc. perform and printing patterns are a grain shank, a grain shank, a texture shank, an alphabetic character, a geometrical pattern, whole surface solid, etc. When there is the need of concealing FRP mold goods, a whole surface solid layer is further prepared in the FRP (SMC) side of a pattern, and the high pigment of concealment nature, such as a titanium dioxide and carbon black, is added in the whole surface solid layer. Printing ink consists of various pigments (or color) and binder resin. A binder is suitably chosen from 2 liquid hardening mold urethane, an acrylic, polyester, a vinyl chloride vinyl acetate copolymer, cellulose system resin, a polyvinyl butyral, etc., and is used. Moreover, as ornament processing, metal thin films, such as aluminum and chromium, may be formed by vacuum evaporation, sputtering, etc. In this case, the shape of the whole surface or a pattern has as a metal thin film. As long as a base material sheet is transparent, the printing pattern layer metallurgy group thin film given as ornament processing may be given to the front face of this sheet, or may be given to a rear face (thermosetting resin side). However, the laminating of the thermoplastics sheet which contains the reactant component of said presentation on this ornament processing is further carried out so that the chemical bond of the component in thermosetting resin and the reactant component in this sheet may not be barred.

[0020] The protective layer which consists of synthetic resin further may be formed on the front face of an ornament sheet if needed. This protective layer chooses a transparent (colorlessness or coloring) thing so that an ornament layer can be looked at through a fluoroscope. When thinking a moldability as important and thinking physical properties, such as surface abrasion-proof nature and chemical resistance, as important as resin, using thermoplastics, hardenability resin, such as thermosetting resin and ionizing-radiation hardenability resin, is used. Although what is necessary is just to decide thickness suitably according to a military requirement, it is usually about 1-100 micrometers. The aforementioned resin is used as thermoplastics. However, when using for a protective layer, it is not necessary to add a reactant component. As thermosetting resin, 2 liquid hardening mold polyurethane resin, an epoxy resin, an unsaturated polyester resin, etc. have the monomer of polyfunctional partial saturation (meta) acrylate, or a typical prepolymer as ionizing-radiation hardenability resin. In addition, as ionizing radiation, ultraviolet rays or an electron ray is usually used.

[0021] As an application of makeup material (mold goods), the interior material of vehicles, such as housing machines, such as interior material of a building, an organ bath, a washstand, and a kitchen instrument, a car, and a vessel, etc. is mentioned.

[0022]

[Example]

(Example 1) The ornament sheet was produced as follows. That is, after carrying out gravure of the pattern to a transparent biaxial extension polyethylene terephthalate sheet ("A4100" by Toyobo, 25-micrometer thickness) using the ink (product made from a THE ink tech "NL-ALFA ink") which uses 2 liquid hardening mold polyurethane as a binder, the adhesives ("E-295" by Dainichiseika Colour & Chemicals Mfg.) of 2 liquid hardening polyurethane resin were used for the printing side, and dry laminate of the acrylonitrile-styrene-butadiene-rubber copolymer sheet ("A403" made from 3 treasure resin industry 200-micrometer thickness) was carried out.

[0023] the ABS side of this ornament sheet — SMC ("RIGORAKU SMC" by Showa High Polymer —) t-butyl par benzoate as a polymerization initiator to an unsaturated-polyester-resin prepolymer 1 % of the weight, Add a styrene monomer as a reactivity [a cross linking agent-cum-] diluent, and naphthenic-acid cobalt is added as a hardening accelerator catalyst 3% of the weight. After installing superposition and these in a die so that what mixed the glass staple fiber 30% of the weight to this may be touched, they are the molding temperature of 150 degrees C, and compacting pressure 90 kgf/cm². While heating and pressurizing for 180 seconds and stiffening SMC, the adhesion unification of both was carried out. Thereby, the makeup material for wall surface panels which carried out die pressing of the shape of tooth to the front face, and used it as it was obtained. There were also no defects of an ornament sheet, such as a tear, and the adhesive property of a Plastic solid and an ornament sheet was also good. Moreover, when exfoliation of an ornament sheet was tried, it fractured in the sheet layer, and it did not exfoliate in the interface of a sheet and a Plastic solid.

[0024] (Example 1 of a comparison) The tissue which carried out gravure of the pattern to the titanium paper ("PM11P" by Kohjin and basis-weight 60 g/m²) into which diallyl phthalate resin was infiltrated using the ink which uses nitrocellulose as a binder was prepared. When fabricated at the same process as the above-mentioned example 1 using this tissue, the tissue was beaten by part for concave heights and it became the makeup material which spoiled the appearance.

[0025] (Example 2) The ornament sheet was produced as follows. That is, after carrying out gravure of the pattern to an acrylic original fabric (the colored acrylic film of a polymethylmethacrylate system, styrene-butadiene-rubber copolymer rubber 20 weight section addition, 50-micrometer thickness) using the ink (product made from Showa ink industry "** X") which uses mixture of an acrylic and a vinyl chloride vinyl acetate copolymer as a binder, the heat welding lamination (doubling embossing) was performed through the transparence acrylic (the transparence acrylic film of a polymethylmethacrylate system, 50-micrometer thickness), and the pattern (ornament) layer in between.

[0026] After installing superposition and these in a die so that the coloring original fabric side of this ornament sheet may touch SMC (thing which made the "SEREKU tea mat" by Takeda Chemical Industries, and the unsaturated-polyester-resin prepolymer system contain a styrene copolymer as a reactant diluent), they are the molding temperature of 145 degrees C, and compacting pressure 86 kgf/cm². While heating and pressurizing for 240 seconds and stiffening SMC, the adhesion unification of both was carried out. Thereby, the makeup panel for bathroom floor lines which carried out the allocated type of the shape of tooth to the front face was obtained. There were also no defects of an ornament sheet, such as a tear, and the adhesive property of a Plastic solid and an ornament sheet was also good. Moreover, when exfoliation of an ornament sheet was tried, it fractured in the sheet layer, and it did not exfoliate in the interface of a sheet and a Plastic solid.

[0027] (Example 2 of a comparison) The ornament sheet was produced as follows. That is, after carrying out gravure of the pattern to a coloring polyvinyl chloride resin sheet (a plasticizer is the diethyl phthalate 20 weight section and 80-micrometer thickness) using the ink (product made from Showa ink industry "** X") which uses mixture of an acrylic and a vinyl chloride vinyl acetate copolymer as a binder, the heat welding lamination (doubling embossing) was performed through the transparence polyvinyl chloride resin sheet (a plasticizer is the diethyl phthalate 20 weight section and 80-micrometer thickness) and the pattern layer in between.

[0028] It fabricated at the same process as an example 2 using this ornament sheet. Although the ornament sheet was not torn in the Plastic solid whole region, when the ornament sheet was exfoliated, it exfoliated in the interface of a sheet and a Plastic solid.

[0029]

[Effect of the Invention] As explained above, according to this invention, the flexibility at the time of heating pressurization and reinforcement are high harder [which is using thermoplastics for a base material sheet], and it can follow it in the shape of [of metal mold] tooth. Moreover, since the molecule of the constituent of thermosetting resin and the molecule of a reactant component carry out a chemical bond by having made the base material sheet contain a reactant component, it can paste up firmly. Furthermore, compared with paper, a nonwoven fabric, etc., clear and delicate printing can be performed to a base material sheet.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is process drawing for explaining the procedure of manufacturing makeup material.

[Description of Notations]

- 1 Ornament Sheet
- 2 Non-Hardened Constituent
- 3 Plastic Solid
- 11 Punch
- 12 Female Mold

[Translation done.]

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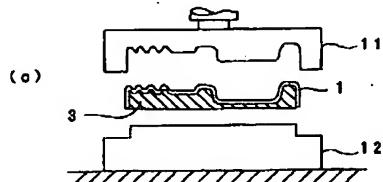
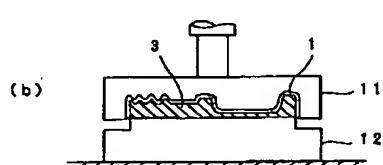
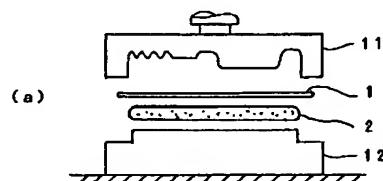
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(54)【発明の名称】 化粧材及びその製造方法

(57)【要約】

【課題】 加熱、加圧時の柔軟性、強度が高く成形性が良好で、鮮明で繊細な印刷をほどこすことができる化粧材を得る。

【解決手段】 熱可塑性樹脂中に熱硬化性樹脂成分分子と付加反応、縮合反応、重付加反応のいずれかにより化学結合し得る単量体或いはプレポリマーを含有する反応性成分を含有する基材シートに装飾処理を施してなる装飾シート1を用意するとともに、熱硬化性樹脂の未硬化物中に繊維質補強材を含有する組成物2を用意し、次いで、これら装飾シート1と未硬化組成物2とを重ね合わせ、所定形状の型11, 12にて加熱、加圧して該組成物を硬化せしめて所定形状の成形体にすると同時に装飾シートと成形体とを接着一体化する。



【特許請求の範囲】

【請求項1】 繊維質補強材で補強された熱硬化性樹脂の硬化物からなる成形体の表面に装飾シートが積層接着されてなり、該装飾シートは熱可塑性樹脂中に熱硬化性樹脂成分分子と付加反応、縮合反応、重付加反応のいずれかにより化学結合し得る有機化合物の単量体或いはプレポリマーからなる反応性成分を含有する基材シートに装飾処理を施したものから構成され、該反応性成分と熱硬化性樹脂成分とがその界面において互いに化学結合してなることを特徴とする化粧材。

【請求項2】 热可塑性樹脂中に熱硬化性樹脂成分分子と付加反応、縮合反応、重付加反応のいずれかにより化学結合し得る単量体或いはプレポリマーからなる反応性成分を含有する基材シートに装飾処理を施してなる装飾シートを用意するとともに、熱硬化性樹脂の未硬化物中に繊維質補強材を含有する組成物を用意し、次いで、これら装飾シートと未硬化組成物とを重ね合わせ、所定形状の型にて加熱、加圧して該組成物を硬化せしめて所定形状の成形体にすると同時に該装飾シートと該成形体とを接着一体化することにより、両者の積層体からなる化粧材となし、かかる後に該積層体を型から取り出すことを特徴とする化粧材の製法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、SMC (Sheet molding compound) 、BMC (Bulk molding compound) 等により成形される化粧材及びその製造方法に関する。

【0002】

【発明が解決しようとする課題】 従来、模様付きの繊維補強熱硬化性化粧材 (FRP) を製造する方法として、チタン紙、不織布、布、含浸紙等を成形同時一体化する方法 (例えば、特開昭48-12876号公報、特開昭51-20951号公報等参照) が知られているが、この方法では、①鮮明な印刷ができない、②破れなどが生じやすい、③成形性がなく形状が制限される、④物理的な投錨効果の接着であるため温度や圧力などの成形条件による接着性のバラツキが大きい、と言った欠点がある。

【0003】 また、特開平7-60911号公報に開示されるように、印刷を施した熔融温度がFRP成形温度以上のプラスチックフィルムに不織布を2液硬化型ウレタン樹脂接着剤にて裏打ちし、このシートを成形時に一体化させるとする方法も採られているが、この方法では裏打ちの工程が複雑である上に地合ムラ等により不織布の品質が不安定であり、コストが高くつくという問題点があった。

【0004】 また別の方法として、特開昭56-72930号公報等に開示されるように、SMC樹脂との接着性の良い、すなわちSMC成形時の温度で熔融又は軟化

するか或いはSMCの成分で膨潤して溶解するプラスチックフィルム乃至は印刷インキを用いた化粧シートを、成形時に一体化させる方法も知られているが、この方法ではSMCの熱硬化時の熱や流動時の応力により印刷層が流されて不良が出るという問題点がある。

【0005】 本発明は、上記のような問題点に鑑みてなされたものであり、その目的とするところは、加熱、加圧時の柔軟性、強度が高く成形性が良く、成形体と装飾シートとの接着も良好で、鮮明で繊細な印刷を施すことができる化粧材及びその製造方法を提供することにある。

【0006】

【課題を解決するための手段】 上記の目的を達成するため、本発明の化粧材は、繊維質補強材で補強された熱硬化性樹脂の硬化物からなる成形体の表面に装飾シートが積層接着されてなり、該装飾シートは熱可塑性樹脂中に熱硬化性樹脂成分分子と付加反応、縮合反応、重付加反応のいずれかにより化学結合し得る有機化合物の単量体或いはプレポリマーからなる反応性成分を含有する基材シートに装飾処理を施したものから構成され、該反応性成分と熱硬化性樹脂成分とがその界面において互いに化学結合してなることを特徴とする。

【0007】 上記の化粧材は、熱可塑性樹脂中に熱硬化性樹脂成分分子と付加反応、縮合反応、重付加反応のいずれかにより化学結合し得る単量体或いはプレポリマーからなる反応性成分を含有する基材シートに装飾処理を施してなる装飾シートを用意するとともに、熱硬化性樹脂の未硬化物中に繊維質補強材を含有する組成物を用意し、次いで、これら装飾シートと未硬化組成物とを重ね合わせ、所定形状の型にて加熱、加圧して該組成物を硬化せしめて所定形状の成形体にすると同時に該装飾シートと該成形体とを接着一体化することにより、両者の積層体からなる化粧材となし、かかる後に該積層体を型から取り出すことにより製造される。

【0008】 上記のように本発明では、熱可塑性樹脂の装飾シート中に熱硬化性樹脂成形体の成分と化学結合する反応性成分を含有せしめ、成形時の硬化反応の際にシートに含有された反応性成分が熱硬化性樹脂と反応接着し一体化できるようにしたものである。

【0009】

【発明の実施の形態】 热可塑性樹脂としては、成形時 (すなわちFRP成形時) の熱 (最大150°C程度) に耐え得るもので、熔融温度 (乃至は融点) がSMC成形温度より高く、尚且つシート成形性の点からはビカット軟化温度がSMC成形温度以下のものが好ましい。また、SMC中の成分により溶解や膨潤のないものを選ぶ。そして基材シートには、用途に応じて隠蔽性又は透明性のあるものが用いられる。具体的には、2軸延伸したポリエチレンテレフタレート (PET) 、ポリブチレンテレフタレート (PBT) 、ポリアリレート等の熱可

塑性ポリエステル、ポリエチレン(PE)、ポリピロピレン(PP)、ポリメチルベンテン、オレフィン系熱可塑性エラストマー等のポリオレフィン、ポリ弗化ビニル、ポリ弗化ビニリデン、エチレン・テトラフルオロエチレン共重合体等の弗素樹脂、シリコン樹脂、ビニロン、ナイロン、ポリ塩化ビニル(PVC)、アクリル、ポリカーボネート、エチレンビニルアルコール共重合体等が挙げられる。これらのシートは単層でも或いは2層以上積層したものを用いてもよい。シート厚みは通常20~300μm程度である。これらのシートの中からSMCの成形温度、成形形状に応じて適当なものを選ぶが、例えば成形温度が150℃、成形形状が平面、又は円筒形等のように曲率を一方向のみに有する曲面の場合には、特に耐熱性及び強度の点から25~200μm厚の2軸延伸PETシートが好適に用いられる。これらの熱可塑性樹脂シートには、必要に応じてコロナ放電処理等の易接着処理や、SMCとの間の空気を抜くための微小孔の穿設等を施してもよい。また、シート自体、或いは直下のFRPの耐候性を向上せしめるため、シート中にベンゾトリアゾール、微粒子酸化セリウム等の紫外線吸収剤、ヒンダードアミン系ラジカル捕捉剤等の光安定剤を添加してもよい。

【0010】反応性成分に含有される有機化合物のうち単量体としては次のものが挙げられる。

- ①スチレン、 α -メチルスチレン、ジビニルベンゼン、ビニルトルエン、酢酸ビニル、(メタ)アクリル酸等のビニル系単量体。
- ②メチル(メタ)アクリレート、2-エチルヘキシル(メタ)アクリレート、フェノキシエチル(メタ)アクリレートなどの単官能(メタ)アクリレート。また、多官能モノマーとして、ジエチレングリコール(メタ)アクリレート、プロピレングリコールジ(メタ)アクリレート、トリメチルプロパントリ(メタ)アクリレート*

*ト、トリメチロールプロパンエチレンオキサイドトリ(メタ)アクリレート、ジベンタエリスリトルペンタ(メタ)アクリレート、ジベンタエリスリトルヘキサ(メタ)アクリレートなど。但し、(メタ)アクリレートとは、アクリレート又はメタアクリレートのこと。

③トリレンジイソシアネート、キシレンジイソシアネート、ヘキサメチレンジイソシアネート、イソホロンジイソシアネート等のイソシアネート。

④その他。

10 【0011】反応性成分に含有される有機化合物のうちプレポリマーとしては次のものが挙げられる。

- ①ウレタン(メタ)アクリレート、ポリエステル(メタ)アクリレート、エポキシ(メタ)アクリレート、トリアジン(メタ)アクリレート等の(メタ)アクリレートプレポリマー。

②前記イソシアネートの付加体、多量体。

③ジアリルフタレートプレポリマー。

④カチオン重合性官能基を有するプレポリマー。例えば、ビスフェノール型エポキシ樹脂、ノボラック型エポキシ化合物等のエポキシ系樹脂、脂肪酸系ビニルエーテル、芳香族系ビニルエーテル等のビニルエーテル系樹脂のプレポリマー。

20 ④その他。

【0012】これらの単量体或いはプレポリマーから、使用する熱硬化性樹脂の未硬化成分分子と付加反応、縮合反応、重付加反応のいずれかの反応により化学結合し得るものを選択する。その組合せの例を表1に示す。その他、一般に熱硬化性樹脂の未硬化物の構成成分の1つと一致するものは有効である。また、これら反応性成分は1種類のみでもよいが、2種類以上を含有させることもできる。

30 【0013】

【表1】

熱硬化性樹脂	反応性有機化合物
不飽和ポリエステル樹脂	スチレン単量体 不飽和ポリエステルプレポリマー
2液硬化型ポリウレタン樹脂	イソシアネート単量体或いはその付加体、多量体
エポキシ樹脂	エポキシ系樹脂プレポリマー
熱硬化性アクリル樹脂	(メタ)アクリレートの単量体 (メタ)アクリレートのプレポリマー

【0014】反応性有機化合物の熱可塑性樹脂シート中の含有の形態としては、混合(相溶化)と共重合の2通りある。混合の代表的な例は、熱可塑性樹脂としてポリ塩化ビニルを、反応性有機化合物として(メタ)アクリレートの単量体或いはプレポリマーを用いた場合であり、両者の混合物を製膜したシート中で、該反応性化合物は未反応時に可塑剤(反応性可塑剤)として機能する

ため、成形性の向上にも寄与する。また、共重合の代表的な例としては、熱可塑性樹脂としてアクリロニトリル-バタジエン共重合体を用い、反応性有機化合物としてスチレン単量体を用い、両者を共重合させてアクリロニトリル-バタジエン-スチレン共重合体とする場合が挙げられる。さらに、共重合体自身が熱可塑性樹脂シートと相溶性がある場合は、該共重合体を熱可塑性樹脂シ

ート中に混合することもできる。例えば、熱可塑性樹脂としてポリメタクリル酸メチルを用い、これにブタジエンースチレン共重合体を混合する場合が挙げられる。

【0015】熱硬化性樹脂としては、不飽和ポリエステル樹脂、ビニールエステル樹脂、ジアリルフタレート樹脂、熱硬化型アクリル樹脂、メラミン樹脂、エポキシ樹脂、2液硬化型ポリウレタン樹脂等が挙げられる。

【0016】これらの熱硬化性樹脂から化粧材（成形品）を作るには、先ずこれらの樹脂の単量体或いはプレポリマー（オリゴマーも包含する）に架橋剤、重合開始剤、或いは反応促進触媒を加えたものに、繊維質補強材とその他必要に応じ各種添加物を加えた未硬化組成物を用意する。この未硬化組成物の形態として例えばSMC又はBMCの形態がある。

【0017】そして、図1（a）に示すように所定形状の成形型（上型11と下型12）の中に装飾シート1と未硬化組成物2とを重ね合わせて挿入し、図1（b）に示す如く型を閉じて加熱、加圧し、未硬化組成物2を架橋乃至は重合させて硬化させることにより、固体の成形体3とすると同時に装飾シート1を成形体3の表面に接着一体化せしめ、図1（c）に示すような化粧材を得る。その際、装飾シート1中の反応性成分と未硬化組成物の分子同士に付加反応、重合反応、重付加反応のいずれかの反応により化学結合を生じせしめ、装飾シート1と成形体3との間の接着力を増強する。

【0018】未硬化組成物の代表的形態であるSMCについて詳述すると、SMCの材料は、ガラス繊維、炭素繊維等の繊維質補強剤、触媒、充填剤、離型剤等を混練した熱硬化性樹脂からなる。用いられる熱硬化性樹脂は通常不飽和ポリエステルのプレポリマーが代表的である。繊維質補強剤としては、通常ガラス繊維の短繊維が用いられる。このガラス繊維の含有量は通常10～70重量%である。充填剤としては、炭酸カルシウム、硫酸バリウム、水酸化アルミニウム等の粉末を用いる。離型剤としてはステアリン酸亜鉛等を用いる。その他、必要に応じてスチレン単量体、多官能アクリレート（又はメタクリレート）単量体等の反応希釈剤、イソシアネート、アミン等の架橋剤、過酸化ベンゾイル、メチルエチルケトンパーオキサイド、tブチルパーエンゾエイト、有機スルホン酸塩等の重合開始剤（硬化触媒）、ナフテン酸コバルト、ナフテン酸マンガン等の硬化促進触媒、二酸化チタン、カーボンブラック等の顔料等を添加する。

【0019】基材シートに施す装飾処理は、該シート自体に染料、顔料等の着色剤を混練して施すことも可能であるが、一般的にはグラビア印刷、シルクスクリーン印刷等により行い、印刷絵柄は、木目柄、石目柄、布目柄、文字、幾何学模様、全面ベタ等である。FRP成形品を隠蔽する必要のある場合は、絵柄のFRP（SMC）側に全面ベタ層を一層設け、その全面ベタ層中に二

酸化チタン、カーボンブラック等の隠蔽性の高い顔料を添加する。印刷インキは各種顔料（又は染料）とバインダー樹脂とからなる。バインダーは、2液硬化型ウレタン、アクリル、ポリエステル、塩化ビニル-酢酸ビニル共重合体、セルロース系樹脂、ポリビニルブチラール等の中から適宜選択して用いる。また装飾処理として、蒸着、スペッタリング等でアルミニウム、クロム等の金属薄膜を形成してもよい。この場合、金属薄膜は全面でもバターン状でもよい。装飾処理として施される印刷絵柄層や金属薄膜は、基材シートが透明であれば、該シートの表面に施しても裏面（熱硬化性樹脂側）に施してもよい。ただし、熱硬化性樹脂中の成分と該シート中の反応性成分との化学結合を妨げないように、該装飾処理上に前記組成の反応性成分を含有する熱可塑性樹脂シートをさらに積層する。

【0020】必要に応じて装飾シートの表面上にさらに合成樹脂からなる保護層を形成してもよい。この保護層は、装飾層を透視可能なように透明（無色或いは着色）なものを選ぶ。樹脂としては、成形性を重視する場合は熱可塑性樹脂を用い、また表面の耐擦傷性、耐薬品性等の物性を重視する場合は熱硬化性樹脂、電離放射線硬化性樹脂等の硬化性樹脂を用いる。厚さは要求性能に応じて適宜決めればよいが、通常1～100μm程度である。熱可塑性樹脂としては前記の樹脂が用いられる。ただし、保護層に用いる場合は反応性成分は添加しなくてもよい。熱硬化性樹脂としては、2液硬化型ポリウレタン樹脂、エポキシ樹脂、不飽和ポリエステル樹脂等が、電離放射線硬化性樹脂としては多官能不飽和（メタ）アクリレートの単量体、又はプレポリマー等が代表的である。なお、電離放射線としては通常紫外線或いは電子線が用いられる。

【0021】化粧材（成形品）の用途としては、建築物の内装材、浴槽、洗面台、厨房器具等の住設器械、車輌、船舶等の乗物の内装材等が挙げられる。

【0022】

【実施例】

（実施例1）装飾シートを次のようにして作製した。すなわち、透明な2軸延伸ポリエチレンテレフタレートシート（東洋紡績製「A4100」、25μm厚）に、2液硬化型ポリウレタンをバインダーとするインキ（ザ・インクテック製「NL-A LF Aインキ」）を用いて絵柄をグラビア印刷した後、その印刷面に2液硬化ポリウレタン樹脂の接着剤（大日精化工業製「E-295」）を用いてアクリロニトリル-ブタジエンースチレン共重合体シート（三宝樹脂工業製「A403」200μm厚）をドライラミネートした。

【0023】この装飾シートのABS面がSMC（昭和高分子製「リゴラックSMC」、不飽和ポリエステル樹脂プレポリマーに重合開始剤としてt-ブチルパーエンゾエイトを1重量%、架橋剤兼反応性希釈剤としてスチ

レン単量体を3重量%、硬化促進触媒としてナフテン酸コバルトを添加し、これにガラス短纖維を30重量%混合したもの)と接するように重ね合わせ、これらを成形型内に設置してから、成形温度150°C、成形圧力90 kgf/cm²で180秒間加熱、加圧してSMCを硬化させるとともに両者を接着一体化させた。これにより、凹凸形状を表面に型押しした壁面パネル用化粧材が得られた。装飾シートの破れ等の不良もなく、成形体と装飾シートの接着性も良好であった。また、装飾シートの剥離を試みたところシート層で破断し、シートと成形体の界面では剥離しなかった。

【0024】(比較例1)ジアリルフタレート樹脂を含浸させたチタン紙(興人製「PM11P」、坪量60g/m²)に、硝化綿をバインダーとするインキを用いて絵柄をグラビア印刷した化粧紙を用意した。この化粧紙を使用して上記実施例1と同じ工程で成形したところ、凹凸部分で化粧紙が破れ、外観を損なった化粧材となつた。

【0025】(実施例2)装飾シートを次のようにして作製した。すなわち、アクリル原反(着色したポリメチルメタクリレート系のアクリルフィルム、ブタジエンスチレン共重合体ゴム20重量部添加、50μm厚)に、アクリルと塩化ビニル酢酸ビニル共重合体の混合物をバインダーとするインキ(昭和インク工業製「化X」)を用いて絵柄をグラビア印刷した後、透明アクリル(ポリメチルメタクリレート系の透明アクリルフィルム、50μm厚)と絵柄(装飾)層を間に介して熱融着ラミネート(ダブリングエンボス)を行った。

【0026】この装飾シートの着色原反側がSMC(武田薬品工業製「セレクティーマット」、不飽和ポリエスチル樹脂プレポリマー系に反応性希釈剤としてスチレン共重合体を含有させたもの)と接するように重ね合わせ、これらを成形型内に設置してから、成形温度145°C、成形圧力86kgf/cm²で240秒間加熱、加圧してSMCを硬化させるとともに両者を接着一体化させた。これにより、凹凸形状を表面に賦型した浴室床面

用化粧パネルが得られた。装飾シートの破れ等の不良もなく、成形体と装飾シートの接着性も良好であった。また、装飾シートの剥離を試みたところシート層で破断し、シートと成形体の界面では剥離しなかった。

【0027】(比較例2)装飾シートを次のようにして作製した。すなわち、着色ポリ塩化ビニル樹脂シート(可塑剤はジオクチルフタレート20重量部、80μm厚)に、アクリルと塩化ビニル酢酸ビニル共重合体の混合物をバインダーとするインキ(昭和インク工業製「化X」)を用いて絵柄をグラビア印刷した後、透明ポリ塩化ビニル樹脂シート(可塑剤はジオクチルフタレート20重量部、80μm厚)と絵柄層を間に介して熱融着ラミネート(ダブリングエンボス)を行った。

【0028】この装飾シートを使用して実施例2と同じ工程で成形した。装飾シートは成形体全域で破れなかつたが、装飾シートを剥離したところ、シートと成形体の界面で剥離した。

【0029】

【発明の効果】以上説明したように、本発明によれば、基材シートに熱可塑性樹脂を使用しているがために、加熱加圧時の柔軟性、強度が高く、金型の凹凸形状に追従することができる。また基材シートに反応性成分を含有させたことにより、熱硬化性樹脂の構成成分の分子と反応性成分の分子とが化学結合するので、強固に接着することができる。さらに、基材シートに対して紙、不織布等に比べ、鮮明で繊細な印刷を施すことができる。

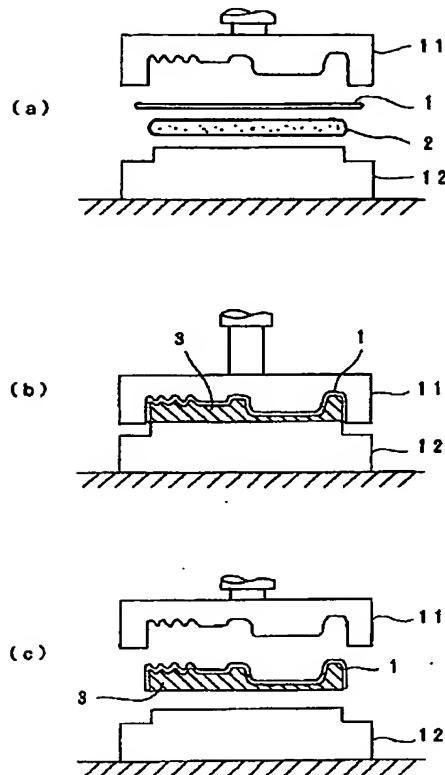
【図面の簡単な説明】

【図1】化粧材を製造する手順を説明するための工程図である。

【30】【符号の説明】

- 1 装飾シート
- 2 未硬化組成物
- 3 成形体
- 11 上型
- 12 下型

【図1】



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